

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-304996

(43)Date of publication of application : 18.10.2002

(51)Int.Cl. H01M 4/60
 C08F 20/36
 H01G 9/00
 H01G 9/035
 H01G 9/04
 H01G 9/042
 H01M 4/02
 H01M 10/40
 // H01M 6/16

(21)Application number : 2001-104629

(22)Date of filing : 03.04.2001

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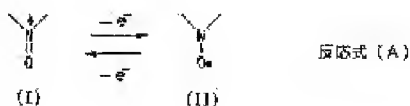
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(54) ELECTRIC STORAGE DEVICE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a new electric storage device having high energy density and usable in a large-current condition.

SOLUTION: This electric storage device includes a nitroxyl compound taking a nitroxyl cation part structure expressed by formula (I) in an oxidized state and taking a nitroxyl radical part structure expressed by formula (II) in a reduced state in a positive electrode, and uses a reaction carrying out the feeding and receiving of electrons between the two states and expressed by reaction formula (A) as the electrode reaction of the positive electrode.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]The energy density of this invention is large and it relates to the accumulation-of-electricity device which can take out a high current at once.

[0002]

[Description of the Prior Art]In connection with rapid market expansions, such as a notebook sized personal computer, a cellular phone, and an electromobile, the high energy density and the accumulation-of-electricity device of a high current which are used for these are called for. Especially, the rechargeable lithium-ion battery which used the lithium containing transition metal oxide for the anode, and used the carbon material for the negative electrode is used for various electronic equipment as a high-energy-density rechargeable battery.

[0003]However, since this rechargeable lithium-ion battery has the small reaction velocity of an electrode reaction, if big current is sent, battery capacity will fall remarkably. Therefore, it was not used for the device which long charging time is needed and needs a high current like an electromobile when it used for sized electronic equipment.

[0004]On the other hand, the electric double layer capacitor which used activated carbon for the electrode can send a high current, and since the cycle characteristic is also excellent, development is furthered as a backup power supply or a power supply for electromobles. However, since the energy density was low, a miniaturization is difficult and was not used for a portable electronic apparatus. Since capacity ran short, it was not widely carried in an electromobile.

[0005]The lead storage battery can send a high current like an electric double layer capacitor, and since the cycle characteristic is also excellent, it is widely used as auxiliary power for cars. However, since voltage was low and the energy density was low, it was not used for the electromobile which performs motorised with electric power.

[0006]

[Problem(s) to be Solved by the Invention]As mentioned above, use by a high current is difficult for a rechargeable lithium-ion battery, and an energy density required for sized electronic equipment is obtained in neither an electric double layer capacitor nor a lead storage battery. That is, in spite of having made the proposal of various accumulation-of-electricity devices as an accumulation-of-electricity device which can be used for a portable electronic apparatus or an electromobile, the accumulation-of-electricity device which an energy density is high and can send a high current was not yet obtained.

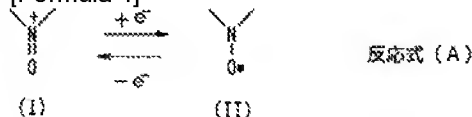
[0007]An object of this invention is to provide the new accumulation-of-electricity device in which an energy density is high and use by a high current is possible.

[0008]

[Means for Solving the Problem]This invention takes nitroxyl cation portion structure shown by formula (I) in an oxidation state, A nitroxyl compound which is shown by formula (II) in reduced condition and takes a nitroxyl radical substructure is contained in an anode, and it is related with an accumulation-of-electricity device using a reaction shown with a reaction formula (A) which delivers and receives an electron between the two states as an electrode reaction of an anode.

[0009]

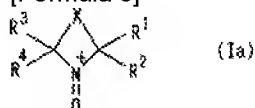
[Formula 4]



As for said nitroxyl compound, it is preferred that it is a compound including the cyclic structure shown by a general formula (Ia) in an oxidation state.

[0010]

[Formula 5]



R¹ - R⁴ express the alkyl group of the carbon numbers 1-4 independently among a formula (Ia), respectively, and X

expresses the divalent basis which forms 5 - 7 membered-ring. Here, a formula (Ia) may be a low molecular weight compound in itself, and may be a part of polymer that X constitutes some side chains of polymer, or by constituting some main chains of polymer.

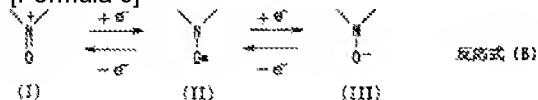
[0011]In particular, it is preferred that said nitroxyl compound is polymer which includes the structure shown by a formula (Ia) in a side chain.

[0012]

[Embodiment of the Invention]The nitroxyl structure can take the state of formula (I) - (III) by electronic transfer, as shown in a reaction formula (B).

[0013]

[Formula 6]



It is made to function as an accumulation-of-electricity device by the electronic accumulation and discharge accompanying it also in it in this invention, using the reaction between formula (I) and (II) as an electrode reaction of an anode. Since this oxidation-reduction reaction is a reaction mechanism without a structural change of an organic compound, it can send current with large therefore reaction velocity and a big accumulation-of-electricity device of this invention at once.

[0014]An accumulation-of-electricity device is a device which can take out the energy which has an anode and a negative electrode at least and was stored electrochemically in the form of electric power here. as an accumulation-of-electricity device -- electric capacity device [, such as a primary battery, a chargeable and dischargeable rechargeable battery; capacitor, and a capacitor,]; -- in addition to this, an electrochemical switching element can be mentioned.

[0015]In the cell which used the conventional metallic oxide etc. for the anode, since a high current was not able to be sent at once, the use as electric capacity devices, such as a capacitor, was difficult, but. The accumulation-of-electricity device of this invention can be conventionally used also as capacitors, such as a backup power supply and a power supply for electromobiles, and the capacitor further for electronic equipment by which the electric double layer capacitor was used. The use as electrochemical switching of an accumulation-of-electricity state using [using a quick charging and discharging characteristic] an ON state and a discharge state as an OFF state is also possible.

[0016]In an accumulation-of-electricity device, an anode is an electrode with a high oxidation-reduction potential, and a negative electrode is an electrode with a conversely lower oxidation-reduction potential.

[0017]In this invention, nitroxyl structure has a preferred annular nitroxyl structure shown by a formula (Ia) in an oxidation state. In reduced condition, a nitroxyl portion of a formula (Ia) has nitroxyl radical structure of formula (II).

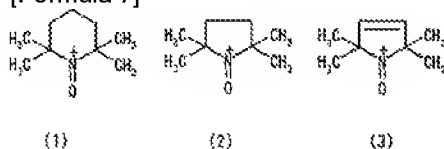
[0018]Especially as $R^1 - R^4$, an alkyl group of straight chain shape is preferred, and a methyl group is preferred especially in respect of radical stability.

[0019]An atom which constitutes a ring member in the basis X is chosen from a group which consists of carbon, oxygen, nitrogen, and sulfur. As the basis X, specifically $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH_2CH_2CH_2CH_2-$, $-CH=CH-$, $-CH=CHCH_2-$, $-CH=CHCH_2CH_2-$, and $-CH_2CH=CHCH_2-$ and in it, $-CH_2-$ not adjoining may be replaced by $-O-$, $-NH-$, or $-S-$, and $-CH=$ may be replaced by $-N=$. A hydrogen atom combined with an atom which constitutes a ring may be replaced by an alkyl group, a halogen atom, $=O$, an ether group, an ester group, a cyano group, amide group, etc.

[0020]A 2, 2, 6, and 6-tetramethyl piperidino KISHIRU cation in which especially a desirable annular nitroxyl structure is shown by a formula (1) in an oxidation state, It is chosen out of a group which consists of a 2, 2, 5, and 5-tetramethyl pyrrolino KISHIRU cation shown by 2, 2 and 5 which are shown by formula (2), and 5-tetramethyl pyrrolidino KISHIRU cation, and a formula (3).

[0021]

[Formula 7]

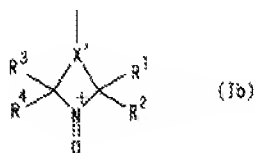


The cyclic structure shown by a formula (Ia) may be a compound of an itself low molecule, or may constitute a part of polymer. When a part of polymer is constituted, it may exist in the side chain, some main chains may be constituted, or whichever may be sufficient. It is more desirable to exist in the side chain from easies, such as composition.

[0022]When it exists in a side chain, as shown in a formula (Ib), it has combined with polymer by residue X' which took hydrogen from $-CH_2-$ which constitutes the ring member in the basis X, $-CH=$, or $-NH-$.

[0023]

[Formula 8]



(R¹ - R⁴ are synonymous with the above among a formula.)

As polymer used, there is no restriction in particular then, and no matter it may be what thing, the cyclic structure of a formula (1a) should just exist in the side chain.

[0024]A part of atoms or bases of the thing which the basis of the formula (1b) specifically added to the next polymer, or polymer can mention what was replaced by the basis of the formula (1b). It is not direct, and in any case, the suitable divalent basis could be passed in the middle, and the basis of a formula (1b) may combine it.

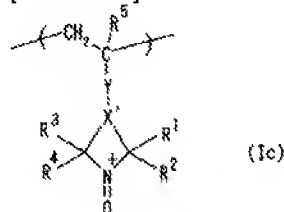
[0025]For example, polyethylene, polypropylene, polybutene, poly decene, Polyalkylene system polymer, such as poly dodecen, a polyheptene, polyisobutene, and poly octadecene; Polybutadiene, Diene system polymer; poly(meta) acrylic acid; poly(meta) acrylonitrile, such as polychloroprene, polyisoprene, and polyisobutene; Poly(meta) acrylamide, Polymethyl(meta) acrylamide, polydimethyl(meta) acrylamide, Poly(meta) acrylamide polymer, such as polyisopropyl(meta) acrylamide; Polymethyl (meta) acrylate, Poly alkyl (meta) acrylate, such as polyethyl (meta) acrylate and polybutyl (meta) acrylate; Polyvinylidene fluoride, Fluorine system polymer, such as polytetrafluoroethylene; Polystyrene, Polystyrene system polymer, such as polybromostyrene, polychlorostyrene, and polymethylstyrene; Polyvinyl acetate, Vinyl system polymer, such as polyvinyl alcohol, polyvinyl chloride, polyvinyl methyl ether, a polyvinyl carbazole, polyvinyl pyridine, and a polyvinyl pyrrolidone; Polyethylene oxide, polypropylene oxide, Polybutene oxide, polyoxymethylene, polyacetaldehyde, The polymethyl vinyl ether, polypropylene pill vinyl ether, polybutylvinyl ether, Polyether system polymer, such as polybenzylvinyl ether; A polymethylene sulfide, A polyethylene sulfide, polyethylene disulfide, a polypropylene sulfide, Polysulfide system polymer, such as a polyphenylene sulfide, polyethylene tetra full FIDO, and a polyethylene trimethylene sulfide; Polyethylene terephthalate, Polyethylene adipate, polyethylene isophthalate, polyethylenenaphthalate, Polyurethane, such as polyester; poly trimethylene ethylene urethane, such as polyethylene REMPORA phenylenediacetate and PORIECHIRENISOPUROPIDENJIBENZOE-TO; Polyether ketone, poly ketone system polymer [, such as polyallyl ether ketone,]; -- polyanhydride system polymer [, such as polyoxy iso phthloyl]; -- polyethylene amine. Polyamide system polymer, such as polyamine system polymer; nylon, such as polyhexamethylene amine and polyethylene trimethylene amine, polyglycine, and a polyalanine; Polyacetyl imino ethylene, Poly imine system polymer, such as polybenzo ylimino ethylene; Polyester imide, Polyimide system polymer, such as polyether imide, polybenzimidazole, and PORIPIRO mel imide; Polyallylene, Polyallylene alkylene, polyallylene alkenylene, polyphenol, Phenol resin, polybenzimidazole, polybenzothiazole, A poly benzoxazine, polybenzoxazole, pollical borane, and polydibenzofuran, Poly oxo isoindoline and diimidepolyfrantetracarboxylate, Polyoxadiazole, poly oxindole, polyphthalazine, poly lid RAIDO, Poly cyanurate, polyisocyanurate, a polypiperazine, polypiperidine, Polypyrazino kino KISAN, a polypyrazole, poly pyridazine, polypyridine, Poly PIROMERI thymine, polyquinone, polypyrrolidine, polyquinoxaline, Polysaccharide, such as poly aromatic system polymer; cellulose, such as polytriazine and polytriazole; Poly disiloxane, siloxane system polymer [, such as poly dimethylsiloxane,]; -- polysilane system polymer; -- polysilazane system polymer; -- polyphosphazene system polymer; -- polythiazyl system polymer; and polyacethylene. Conjugated system polymer, such as polypyrrole and poly aniline, can be mentioned.

[0026]Polyalkylene system polymer, poly(meta) acrylic acid, poly(meta) acrylamide polymer, poly alkyl (meta) acrylate, and polystyrene system polymer are preferred at a point of excelling in tolerance with an electrochemical main chain in this. A main chain is a chain with most carbon numbers in a high molecular compound.

[0027]It is preferred that polymer is chosen so that a unit shown by a formula (1c) by an oxidation state can be included also in this.

[0028]

[Formula 9]

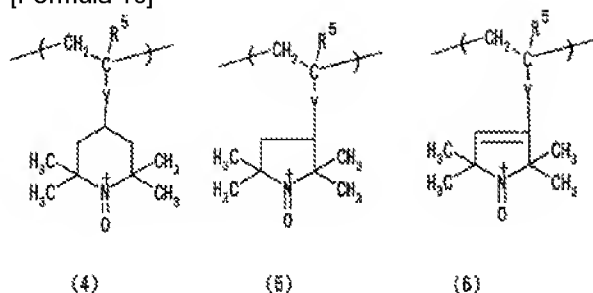


Here, R⁵ is hydrogen or a methyl group. Although Y does not have limitation in particular, -CO-, -COO-, -CONR⁶-, -The alkylene group of the carbon numbers 1-18 which may have O-, -S-, and a substituent, the allylene group of the carbon numbers 1-18 which may have a substituent, and the divalent basis which combined two or more of these bases can be mentioned. R⁶ expresses hydrogen or the alkyl group of the carbon numbers 1-18.

[0029]It is a unit expressed with a formula (1c), and especially a desirable thing is expressed with following formula (4) - (6).

[0030]

[Formula 10]



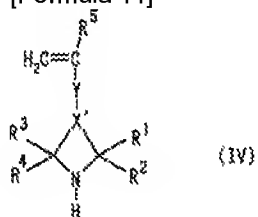
Formula (4) In - (6), $-\text{COO}-$ and $-\text{CONR}^6-$ are preferred especially as Y.

[0031]In this invention, the basis of a formula (Ib) does not need to exist in all the side chains. For example, even if all the units that constitute polymer are units shown by a formula (Ic), a part may be a unit shown by a formula (Ic), or any may be sufficient. Although it differs in the purpose, the structure of polymer, and a manufacturing method, how much it is contained in polymer should just exist, even when it is small, and especially 10 % of the weight or more is usually preferred [or] 1 % of the weight or more 0.1 % of the weight or more. There is no restriction in particular in polymer synthesis, and 80 % of the weight or more is especially preferred 50 % of the weight or more to obtain the biggest possible accumulation-of-electricity operation.

[0032]In order to compound such polymer, after obtaining polymer by copolymerization with the monomer to which homopolymerization or alkyl acrylate can carry out copolymerization of the monomer shown, for example by formula (IV), - By oxidizing and converting NH-portion into $-\text{N(O)}-$, the polymer which has a unit shown by a formula (Ic) in an oxidation state can be obtained.

[0033]

[Formula 11]



After compounding the polymer which polymerizes methacrylic acid etc. and serves as a base, for example, the basis (or basis which has $-\text{NH}-$ before oxidizing to NO radical) shown by a formula (Ib) by a polymeric reaction may be introduced.

[0034]When the accumulation-of-electricity device of this invention has an electrolyte containing a solvent, it is preferred that a nitroxyl compound does not dissolve in an electrolyte, i.e., endurance is high. Therefore, although the molecular weight of polymer including the annular nitroxyl structure of a formula (Ia) does not have restriction in particular, it is preferred to have only a molecular weight which cannot be solved to an electrolyte, and this changes with combination with the kind of organic solvent in an electrolyte. Generally, it is 1,000 or more molecular weights, and is 100,000 or more 10,000 or more especially preferably. Since it is mixable to an anode as a granular material in this invention, a molecular weight may be large how much. Generally, it is 5,000,000 or less molecular weight. Polymer including the annular nitroxyl structure of a formula (Ia) may be constructing the bridge, and, thereby, can raise the endurance to an electrolyte.

[0035]A nitroxyl cation of formula (I) is usually stabilized with an electrolytic anion. Specifically, PF_6^- , ClO_4^- , BF_4^- , Br^- , Cl^- , F^- , an imide system electrolyte salt anion, a methide system electrolyte salt anion, etc. can be mentioned.

[0036]Main functions of a nitroxyl compound in an anode are roles of an active material contributed to accumulation of electricity. Therefore, the whole quantity of positive active material of the conventional accumulation-of-electricity device, for example, the conventional cell, can be transposed to a nitroxyl compound specified by this invention. Since a high current can be sent so much even if it replaces some conventional active materials, quantity in the whole active material does not have restriction in particular. To the whole active material, if it is 0.1 % of the weight or more, it is so much effective, and if it is 10 % of the weight or more, an effect will fully be seen. 50 % of the weight or more, it is 80 % of the weight or more and it is also especially preferred to consider it as 100 % of the weight to obtain the biggest possible accumulation-of-electricity operation. Since this nitroxyl compound makes a component elements with a small atomic weight, such as carbon, hydrogen, nitrogen, and oxygen, it can be stored electricity for many electric charges by small weight. Therefore, a high-energy-density accumulation-of-electricity device is realized.

[0037]Although a publicly known thing is used as a conventional active material, metallic oxides, such as LiMnO_2 , LiCoO_2 , LiNiO_2 , or $\text{Li}_x\text{V}_2\text{O}_5$ ($0 < x < 2$), can be mentioned, for example.

[0038]In addition to an active material, in an anode, a publicly known thing can be conventionally contained as other constituents. As such a thing, conductive polymers, such as carbon materials, such as activated carbon, graphite, carbon black, and acetylene black, polyacetylene, polyphenylene, poly aniline, and polypyrrole, are mentioned as an electric conduction adjuvant, for example. Resin, such as polyvinylidene fluoride, polytetrafluoroethylene, a vinylidene fluoride

hexafluoropropylene copolymer, styrene butadiene rubber, polypropylene, polyethylene, and polyimide, can be mentioned as a binder. In addition, a compound, ion conductivity polymers, etc. in which a disulfide compound and a catalytic effect are shown may be contained suitably.

[0039]When a nitroxyl compound is polymer, it can serve as a function of a binder according to a kind of main chain of polymer, a kind of side chain with which annular nitroxyl structure is added, or a kind of side chain which does not have annular nitroxyl structure. In that case, use of the conventional binder can become unnecessary or the amount of the conventional binder used can be reduced. Or the conventional active material may be used as it is, polymer which has annular nitroxyl structure may be used as a binder, and since quantity which is equivalent to a binder in that case will function also as an active material, high capacity-ization can be attained so much.

[0040]When a main chain of polymer consists of conductive polymers, such as polyacetylene and poly aniline, and annular nitroxyl structure exists in the side chain, polymer which has annular nitroxyl structure can serve as an electric conduction adjuvant. In this case, use of the conventional electric conduction adjuvant can become unnecessary, or the amount of the conventional electric conduction adjuvant used can be reduced. Or the conventional active material may be used as it is, polymer which has annular nitroxyl structure may be used as an electric conduction adjuvant, and since quantity which is equivalent to an electric conduction adjuvant in that case will function also as an active material, high capacity-ization can be attained so much.

[0041]It is thought that nitroxyl cation structure also has work which inactivates impurities contained, for example in an electrolyte, such as water and alcohol, and it is serving to control performance degradation of an accumulation-of-electricity device.

[0042]When a nitroxyl compound is polymer, in any case, solubility over an electrolyte containing an organic solvent etc. is low, and especially since endurance is high, an effect is large [a case].

[0043]an accumulation-of-electricity device of this invention -- an above-mentioned anode -- at least -- a negative electrode -- it has an electrolyte preferably. One example of the structure is shown in drawing 1. An accumulation-of-electricity device shown in a figure has the composition which piled up the negative electrode 3 and the anode 5 via the separator 4 containing an electrolyte. However, since an accumulation-of-electricity device in this invention is an accumulation-of-electricity device which makes the negative electrode 3 and the anode 5 a component at least, the negative pole collector 1, the insulating packing 2, the separator 4, and the positive pole collector 6 are not necessarily required.

[0044]Publicly known shape can be used for shape of an accumulation-of-electricity device. As an accumulation-of-electricity device-shaped example, what closed a layered product or a winding body of an electrode with metal casing, a resin case, or a laminate film is mentioned. As appearance, cylindrical, a square shape, a coin type, a sheet type, etc. are mentioned.

[0045]As a negative electrode, a publicly known thing can be conventionally used as an accumulation-of-electricity device-electrodes material. For example, carbon materials, such as activated carbon, graphite, carbon black, and acetylene black, Conductive polymers, such as a lithium metal or a lithium alloy, lithium ion occlusion carbon, various kinds of other metal simple substances or an alloy, polyacetylene, polyphenylene, poly aniline, and polypyrrole, can be used. Polyvinylidene fluoride, polytetrafluoroethylene, a vinylidene fluoride hexafluoropropylene copolymer, A compound, ion conductivity polymers, etc. in which resin binders, such as styrene butadiene rubber, polypropylene, polyethylene, and polyimide, other disulfide compounds, and a catalytic effect are shown can be made to contain suitably.

[0046]As construction material of the negative pole collector 1 and the positive pole collector 6, nickel, aluminum, copper, gold, silver, titanium, an aluminum alloy, stainless steel, a carbon raw material, etc. can be mentioned. A thing of foil, a plate, and mesh state can be used as shape. A catalytic effect may be given to a charge collector or the chemical bond of an active material and the charge collector may be carried out. A separator and a nonwoven fabric which consist of a porosity film can be used for an accumulation-of-electricity device in this invention in order to prevent electric interengagement of the negative electrode 3 and the anode 5. On the other hand, the insulating packing 2 which consists of plastic resin can be used in order to prevent electric interengagement of the negative pole collector 1 and the positive pole collector 6.

[0047]An electrolyte can be used for an accumulation-of-electricity device of this invention. An electrolyte performs electrification mediated transport between a negative electrode and an anode, and, generally has the electrolytic ion conductivity of 10^{-5} - 10^{-1} S/cm at a room temperature. As an electrolyte in this invention, an electrolysis solution which dissolved electrolyte salt in a solvent, for example can be used. As such a solvent, for example Ethylene carbonate, propylene carbonate, Dimethyl carbonate, diethyl carbonate, methylethyl carbonate, Organic solvents, such as gamma-butyrolactone, a tetrahydrofuran, dioxolane, sulfolane, dimethylformamide, dimethylacetamide, and N-methyl-2-pyrrolidone, or sulfuric acid solution, water, etc. are mentioned. this invention -- these solvents -- it can be independent, or two or more kinds can be mixed, and it can also use. When using an organic solvent especially, endurance can be raised by using a nitroxyl compound which is polymer.

[0048]As electrolyte salt, for example LiPF_6 , LiClO_4 , LiBF_4 , LiCF_3SO_3 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$, $\text{LiC}(\text{CF}_3\text{SO}_2)_3$, $\text{LiC}(\text{C}_2\text{F}_5\text{SO}_2)_3$, LiBr , LiCl , LiF , etc. are mentioned.

[0049]In structure of an accumulation-of-electricity device shown in drawing 1, it is used for it, including an electrolyte in the separator 4.

[0050]A solid electrolyte may be used as an electrolyte. As organic solid electrolyte materials, among these solid electrolytes, Vinylidene fluoride system polymers, such as polyvinylidene fluoride and a fluoridation vinylidene-hexafluoropropylene copolymer, Acrylic nitrile system polymers, such as an acrylonitrile methyl methacrylate copolymer and an acrylonitrile methyl acrylate copolymer, polyethylene oxide, etc. are mentioned. These polymer materials may include an

electrolysis solution, may be made into gel, and may be used, or only a polymeric material may be used for them as it is. On the other hand, as an inorganic solid electrolyte, CaF_2 , AgI , LiF , beta-alumina, a glass material, etc. are mentioned. When using such a solid electrolyte, it is not necessary to use a separator.

[0051]As a manufacturing method of an anode, a publicly known method can be used conventionally. For example, a method of adding a solvent to a component, making into slurry form, and applying to an electrode collector, a method of adding binder resin and hardening, putting it, a method of burning [applying it] and hardening heat, etc. are mentioned. In that case, as for a nitroxyl compound, distributing in an anode uniformly is preferred, and when insoluble to a solvent, it is preferred to grind and use it.

[0052]A thing of an oxidation state which has a cation shown by formula (I) also by a thing of reduced condition which has a radical shown by formula (II) as a nitroxyl structure of using when manufacturing an anode may be used.

[0053]

[Example]Hereafter, an example explains this invention concretely.

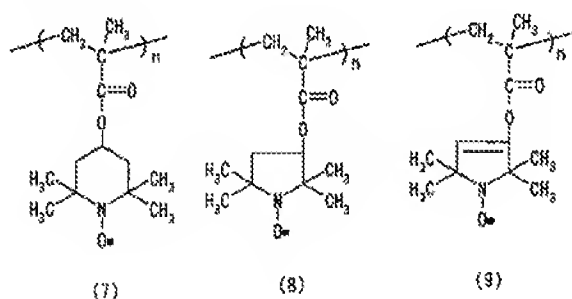
[0054]In the 100-ml eggplant flask which attached the <example of composition of annular nitroxyl structure content polymer> refluxing pipe, it is 2,2,6,6-tetramethylpiperidine. Methacrylate 20 g (0.089 mol) of monomers were put in, and it was made to dissolve in 80 ml of dry tetrahydrofurans. There, 0.29 g (0.00187 mol) (monomer/azobisisobutyronitrile=50/l) of azobisisobutyronitrile (azobisisobutyronitrile) was added there, and it stirred at 75-80 °C under argon atmosphere. It cooled radiationally to the room temperature after a 6-hour reaction. In hexane, polymer was deposited, it filtered, reduced pressure drying was carried out, and 18 g (90% of yield) of poly (2, 2, 6, and 6-tetramethylpiperidine methacrylate) was obtained.

[0055]Next, 10 g of obtained poly (2,2,6,6-tetramethylpiperidine methacrylate) was dissolved in 100 ml of **** dichloromethane. It was dropped over 1 hour, stirring 100 ml of dichloromethane solutions of m-chloroperbenzoic acid 15.2g (0.088 mol) at a room temperature here. Precipitating m-chlorobenzoic acid was filtered and removed after 6 more hour stirring, and dichloromethane was distilled off for filtrate after washing with sodium carbonate solution and water. The powder obtained by grinding the solid content which remained was washed by diethyl carbonate (DEC), was dried under decompression, and 7.2 g of poly (2, 2, 6, and 6-tetramethyl piperidino KISHIMETAKURI rate) (PTME) shown with a following formula (7) was obtained (68.2% of yield, blackish brown powder). The structure of the obtained polymers was checked by IR. As a result of measuring by GPC, a value called weight-average-molecular-weight $M_w=89000$ and degree-of-dispersion $M_w/M_n=3.30$ was obtained. The spin concentration for which it asked with the ESR spectrum was 2.51×10^{21} spin/g. A poly (2, 2, 6, and 6-tetramethylpiperidine methacrylate) N-H group is converted 100% to a N-O radical, and this corresponds with spin concentration when all the monomeric units of this polymer assume that it has a radical.

[0056]Similarly, the poly (2,2,5,5-tetramethyl pyrrolidino JINOKISHI methacrylate) shown with a following formula (8) and the poly (2, 2, 5, and 5-tetramethyl pyrrolidino NOKISHI methacrylate) shown by a formula (9) were compounded.

[0057]

[Formula 12]



<Example 1> 200 mg of graphite powder and 25 mg of polytetrafluoroethylene resin binders were measured and taken, and it mixed with 25 mg of polymethacrylate of the compound formula (7) with the agate mortar. The pressure was put, roller extension of the mixture produced by carrying out dry blending about 10 minutes was carried out, and the 215-micrometer-thick thin electrode board was obtained. After drying at 80 °C among a vacuum overnight, the thin electrode board was struck to a round shape 12 mm in diameter, and was molded as a coin cell and an electrode for accumulation-of-electricity devices. The gross weight of an electrode is 14.4 mg and the polymethacrylate of a 1.44 mg (10 % of the weight) formula (7) is contained in this. The bulk density of the electrode was 0.533 g/cm^3 .

[0058]Next, the obtained electrode was dipped in the electrolysis solution and the electrolysis solution was infiltrated into the opening in an electrode. As an electrolysis solution, the ethylene carbonate / diethyl carbonate mixed solution (mixture ratio 3:7) containing the LiPF_6 electrolyte salt of 1 mol/l were used. The electrode impregnated with the electrolysis solution was placed on the positive pole collector, and the porosity film separator impregnated with the electrolysis solution the same on it was laminated. The lithium metal board which furthermore serves as a negative electrode was laminated, and the negative pole collector covered with insulating packing was piled up. In this way, the pressure was applied for the made layered product with the caulking machine, and the coin type accumulation-of-electricity device of the encapsulated type was obtained.

[0059]The reversible electrode potential of the accumulation-of-electricity device produced as mentioned above was 2.7V. Next, to the obtained accumulation-of-electricity device, it charged by 1 mA of constant current, and when voltage rose to

4.0V, charge was ended. When the accumulation-of-electricity device after charge was disassembled and the anode was analyzed, reduction in radical concentration was observed and generation of the corresponding 2, 2, 6, and 6-tetramethyl piperidino KISHIRU cation was checked. This cation is stabilized by electrolyte anion PF_6^- .

[0060]The accumulation-of-electricity device was produced similarly and it charged by 1 mA of constant current, and immediately after voltage rose to 4.0V, it discharged. Discharge current is 1 mA of constant current as well as the time of charge. The charge in that case and a discharge curve are shown in [drawing 2](#). At the time of discharge, the voltage flat part was observed in the 3.6V neighborhood. It turned out that this voltage flat part is equivalent to the potential difference between the reduction reaction which changes from the nitroxyl cation which has happened with the anode to a nitroxyl radical, and the ionization reaction of a lithium metal which has occurred with the negative electrode. That is, this is the result of the accumulation-of-electricity device by this example 1 showing that it is operating as a chemical cell.

[0061]The capacity of the accumulation-of-electricity device measured by this example 1 was 55.6mAh per anode 1g per 5.56mAh and 1g of polymethacrylate. This capacity is equivalent to 50% of the theoretical capacity of polymers.

[0062]The accumulation-of-electricity device was produced similarly and the charge and discharge by 1 mA were repeated. It carried out until charge was set to 4.0V and discharge was set to 3.0V. Change of the service capacity at the time of repeating a cycle 100 times is shown in [drawing 3](#). Even if it repeated charge and discharge, capacity did not decrease. That is, this accumulation-of-electricity device was understood that repetition charge and discharge are possible over a long period of time.

[0063]An accumulation-of-electricity device is produced still more nearly similarly, and the discharge curve at the time of performing charge and discharge with the discharge rates 1C, 2C, 5C, 10C, and 30C is shown in [drawing 4](#). It carried out until charge was set to 4.2V and discharge was set to 2.5V. It turned out that the accumulation-of-electricity device in this invention shows 70% of capacity in the case of the discharge rate 1C (they are full charge and full discharge in 1 hour) also in the case of the discharge rate 30C (they are full charge and full discharge at 2 minutes). That is, this result shows that the characteristic does not deteriorate easily, even when the accumulation-of-electricity device by this example carries out charge and discharge by a high current.

[0064]The accumulation-of-electricity device which does not contain an organic polymer compound with annular nitroxyl structure in an anode as comparison of the example in <comparative example 1> this invention was produced. First, 225 mg of graphite powder and 25 mg of polytetrafluoroethylene resin binders are measured and taken, and it mixes with an agate mortar. After it, the electrode was produced by the same method as Example 1, and the accumulation-of-electricity device was assembled using the same electrolyte as Example 1, the separator, the positive pole collector, and the negative pole collector.

[0065]The reversible electrode potential of the accumulation-of-electricity device produced as mentioned above was 2.9V. Next, it charged by 1 mA of constant current, to the obtained accumulation-of-electricity device, when voltage rose to 4.0V, charge was ended, and it discharged by 1 mA of constant current the same immediately after that. The result is shown in [drawing 2](#). The voltage of the accumulation-of-electricity device changed in drops almost linearly, and the voltage flat part checked in Example 1 was not checked. The voltage which changes in drops is equivalent to the potential difference between the potential of the electric double layer ingredient stored in the graphite powder surface, and the ionization reaction of a lithium metal which has occurred with the negative electrode, then is considered. However, the capacity was small and was anode 1g per 0.64mAh.

[0066]<Example 2> 200 mg of graphite powder and 25 mg of polytetrafluoroethylene resin binders were measured and taken, and it mixed with 25 mg of polymethacrylate shown by the compound formula (8) with the agate mortar. After it, the electrode was produced by the same method as Example 1, and the accumulation-of-electricity device was assembled using the same electrolyte as Example 1, the separator, the positive pole collector, and the negative pole collector.

[0067]The reversible electrode potential of the accumulation-of-electricity device produced as mentioned above was 2.7V. Next, to the obtained accumulation-of-electricity device, it charged by 1 mA of constant current, and when voltage rose to 4.0V, charge was ended. When the accumulation-of-electricity device after charge was disassembled and the anode was analyzed, reduction in radical concentration was observed and generation of the corresponding 2, 2, 5, and 5-tetramethyl pyrrolidino KISHIRU cation was checked. This cation is stabilized by electrolyte anion PF_6^- .

[0068]The accumulation-of-electricity device was produced similarly and it charged by 1 mA of constant current, and immediately after voltage rose to 4.0V, it discharged. Discharge current is 1 mA of constant current as well as the time of charge. As a result, the voltage flat part was accepted at the time of discharge. It turned out that this voltage flat part is equivalent to the potential difference between the reduction reaction which changes from the nitroxyl cation which has happened with the anode to a nitroxyl radical, and the ionization reaction of a lithium metal which has occurred with the negative electrode. That is, this is the result of the accumulation-of-electricity device by this example 2 showing that it is operating as a chemical cell.

[0069]It turned out that the accumulation-of-electricity device obtained by this example 2 has the capacity of 56.1mAh per anode 1g per 5.61mAh and 1g of polymethacrylate. Like Example 1, repetition charge and discharge were possible over a long period of time, and even when charge and discharge were carried out by a high current, it was checked that the characteristic does not deteriorate easily.

[0070]<Example 3> 200 mg of graphite powder and 25 mg of polytetrafluoroethylene resin binders were measured and taken, and it mixed with 25 mg of polymethacrylate shown by the compound formula (9) with the agate mortar. After it, the electrode was produced by the same method as Example 1, and the accumulation-of-electricity device was assembled using

the same electrolyte as Example 1, the separator, the positive pole collector, and the negative pole collector.

[0071]The reversible electrode potential of the accumulation-of-electricity device produced as mentioned above was 2.7V. Next, to the obtained accumulation-of-electricity device, it charged by 1 mA of constant current, and when voltage rose to 4.0V, charge was ended. When the accumulation-of-electricity device after charge was disassembled and the anode was analyzed, reduction in radical concentration was observed and generation of the corresponding 2, 2, 5, and 5-tetramethyl pyrrolino KISHIRU cation was checked. This cation is stabilized by electrolyte anion PF_6^- .

[0072]The accumulation-of-electricity device was produced similarly and it charged by 1 mA of constant current, and immediately after voltage rose to 4.0V, it discharged. Discharge current is 1 mA of constant current as well as the time of charge. As a result, the voltage flat part was accepted at the time of discharge. It turned out that this voltage flat part is equivalent to the potential difference between the reduction reaction which changes from the nitroxyl cation which has happened with the anode to a nitroxyl radical, and the ionization reaction of a lithium metal which has occurred with the negative electrode. That is, this is the result of the accumulation-of-electricity device by this example 3 showing that it is operating as a chemical cell.

[0073]It turned out that the accumulation-of-electricity device obtained by this example 3 has the capacity of 5.69mAh per anode 1g per 56.9mAh and 1g of polymethacrylate. Like Example 1, repetition charge and discharge were possible over a long period of time, and even when charge and discharge were carried out by a high current, it was checked that the characteristic does not deteriorate easily.

[0074]

[Effect of the Invention]According to this invention, the accumulation-of-electricity device which can send a high current with high energy density can be provided. When a nitroxyl compound is polymer, high endurance is obtained especially.

[Translation done.]

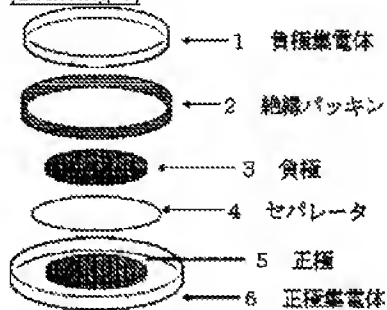
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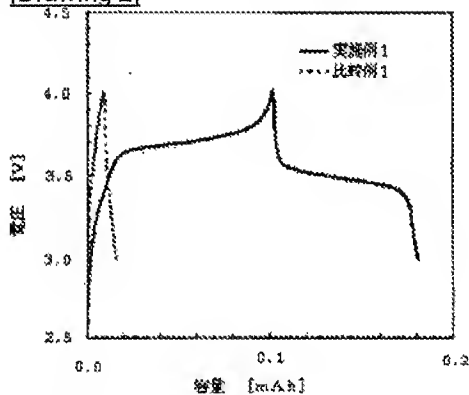
- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DRAWINGS

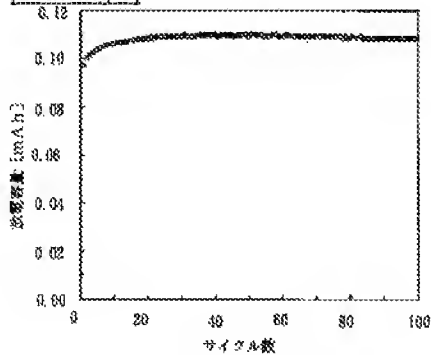
[Drawing 1]



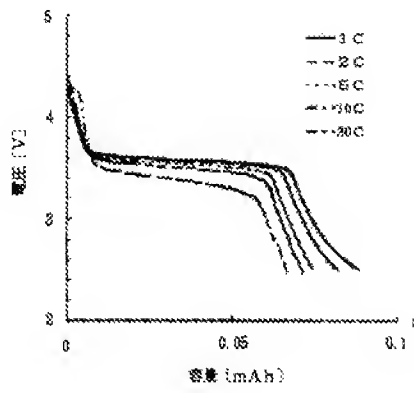
[Drawing 2]



[Drawing 3]



[Drawing 4]



[Translation done.]